FABRICATION OF NANOROD TIO_2/CU_2O HETEROSTRUCTURE THIN FILM

FADILAH NORAZNI BINTI FAHRIZAL

A thesis submitted in
fulfillment of the requirement for the award of the
Degree of Master of Electrical Engineering

Faculty of Electrical and Electronic Engineering
Universiti Tun Hussein Onn Malaysia

AUGUST 2019

DEDICATION

To my parents,

The reason of what I become today

Thanks for your good support and continuous love

To my 9 angels, EXO

You have been my inspirations and my pillar of strengths

EXO, Let's Love

To my beloved mutuals and friends,

Thank you for your endless support and understandings

To my dear self,

You've done great and I'm so proud of you

ACKNOWLEDGEMENT

In the name of Allah, the Most gracious and the Most Merciful

Alhamdulillah, all praises to Allah for the strengths and His blessing in completing this thesis. I would like to express my gratitude and appreciation to all those who gave me the opportunity to complete this thesis. A special thanks to my project supervisor, Dr Fariza Binti Mohamad, who gives a lot of guidance's and suggestions during coordinating my project especially in experiment and maintains project's progress in track.

I would also like to acknowledge with much appreciation to the crucial staff of Microelectronic and Nanotechnology Shamsuddin Research Centre (MiNT-SRC), who gave the permission to use all the required machinery and the necessary material to complete the project. Thanks also to lecturers and panels who gives constructive comments especially in my project presentation that help me to improve my presentation skills.

Last but not least, my deepest gratitude goes to all my friends for their kindness and moral support during my study. To those who indirectly contributed in this project, all of your kindness means a lot to me. Thank you very much.

ABSTRACT

Titanium Dioxide (TiO_2) has been investigated as a potential material to use in solar cell application. It has good refractive index in visible region, able to function as photocatalyst and produces high transmittance. In this study, the chemical stability of TiO_2 and the photon absorbance spectrum of Copper Oxide (Cu_2O) were coupled with their conveniently aligned interface to form a TiO_2 /Cu_2O heterojunction. However, it was reported that, the combination of planar n-type TiO_2/p-type Cu_2O was having low efficiency in solar cell application due to the limited area of the heterostructure for efficient charge collection. Therefore, nanorod structure has been suggested to overcome this problem. Nanorods provide stable electrodes and larger surface area for charge transfer reactions. This approach will attribute the enhancement desirable absorption of UV–visible light in natural solar spectrum which improved the surface–interface reactions. The n-TiO_2 and p-Cu_2O thin film were fabricated using hydrothermal and electrodeposition method, respectively. The fabrication parameters were investigated to obtain the optimum parameters of TiO_2 thin film. The TiO_2 thin film exhibited optimum 16 hours duration of hydrothermal process with the concentration of TBOT used was 0.05 M. After that, p-Cu_2O layer was deposited on nanorod TiO_2 thin film for heterojunction formation. Prior to the p-Cu_2O deposition on nanorod TiO_2/FTO substrate, cyclic voltammetry (CV) measurement was carried out. The p-Cu_2O thin film was deposited at -0.4V vs. Ag/AgCl based on the CV measurement result. The effect of deposition time was also investigated during electrodeposition to improve the properties of the p-n junction semiconductor material. P-Cu_2O thin film were fabricated by using copper acetate based solution through potentiostatic with pH value of 12.5. The Cu_2O was successfully developed on the TiO_2 layer with high crystallinity and lower resistance via two-step electrodeposition method. The successful fabrication of nanorods TiO_2/Cu_2O heterojunction thin film will open a new door of development thin film solar cell application.

ABSTRAK

TiO_2 telah dikaji sebagai bahan yang berpotensi digunakan dalam aplikasi sel solar. Ia mempunyai indeks biasan yang baik di rantau yang kelihatan, keupayaan berfungsi sebagai '*photocatalyst*' dan memberikan transmisi tinggi. Dalam kajian ini, kestabilan kimia TiO_2 dan spektrum penyerapan foton Cu_2O digabungkan dengan antara muka yang sesuai untuk membentuk TiO_2 / Cu_2O heterosimpang. Walau bagaimanapun, dilaporkan bahawa, gabungan jenis planar n-jenis TiO_2/p-jenis Cu_2O mempunyai kecekapan yang rendah dalam aplikasi sel solar disebabkan oleh kawasan heterostruktur terhad untuk pengumpulan caj yang cekap. Oleh itu, struktur nanorod telah dicadangkan untuk memerangi masalah ini. Nanorod menyediakan elektrod yang stabil dan kawasan permukaan yang lebih besar untuk tindak balas pemindahan caj. Pendekatan ini akan mengaitkan peningkatan penyerapan cahaya yang boleh dilihat UV dalam spektrum solar semulajadi yang meningkatkan tindak balas permukaan-permukaan. Filem n-TiO_2 dan p-Cu_2O dibuat menggunakan kaedah hidrotermal dan elektrodeposisi. Parameter fabrikasi diselidik untuk mendapatkan parameter optimum TiO_2 tipisan nipis. Tipisan nipis TiO_2 mempamerkan parameter optimum selama tempoh 16 jam proses hidrotermal dengan kepekatan TBOT yang digunakan ialah 0.05 M. Selepas itu, lapisan p-Cu_2O disimpan pada tipisan nipis nanorod TiO_2 untuk pembentukan heterosimpang. Sebelum pemendapan p-Cu_2O pada nanorod TiO_2 / FTO substrat, pengukuran voltammetri kitaran (CV) telah dijalankan. Tipisan nipis p-Cu_2O didepositkan pada -0.4 vs Ag / AgCl berdasarkan keputusan pengukuran CV. Kesan masa pemendapan juga disiasat semasa elektrodeposisi untuk memperbaiki sifat bahan semikonduktor persimpangan p-n. Tipisan nipis P-Cu_2O dibuat dengan menggunakan penyelesaian berasaskan tembaga asetat melalui potentiostatic dengan nilai pH 12.5. Cu_2O berjaya dibangunkan pada lapisan TiO_2 dengan kristalografi yang tinggi dan rintangan yang lebih rendah. Kejayaan fabrikasi nanorods TiO_2 / Cu_2O heterosimpang tipisan nipis akan membuka pintu baru pembangunan aplikasi sel solar tipisan nipis.

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LIST OF SYMBOLS AND ABBREVIATIONS

Ω	-	Ohm
µm	-	Micrometer
I	-	Current
°	-	Degree
°C	-	Degree Celsius
eV	-	Electronvolt
ρ	-	Resistivity
V	-	Voltage
A	-	Absorbance
Au	-	Gold
a.u	-	Arbitrary unit
AFM	-	Atomic Force Microscope
Ag/AgCl	-	Silver/Silver Chloride
CE	-	Counter electrode
Cm	-	cm
CO_2	-	Carbon dioxide
Cu	-	Copper
Cu_2O	-	Cuprous Oxide
$CuSO_4$	-	Copper sulphate
CV	-	Cyclic voltammetry
DI	-	Deionized
DUT	-	Device Under Test
e	-	Electron
E_g	-	Energy bandgap
FE-SEM	-	Field Emission Scanning Electron Microscope
FTO	-	Fluorine doped tin oxide
ITO	-	Indium doped tin oxide

KOH	-	Pottasium hydroxide
LA	-	Lactic acid
M	-	Mol
mA	-	miliAmpere
Mg	-	Magnesium
NaOH	-	Sodium hydroxide
nm	-	nanometer
Pt	-	Platinum
PV	-	Photovoltaic
RE	-	Reference electrode
TiO_2	-	Titanium dioxide
TCO	-	Transparent coating oxide
UV	-	Ultraviolet
UV-Vis	-	Ultraviolet and Visible absorption spectroscopy
vs	-	Versus
WE	-	Working electrode
XRD	-	X-ray Diffractometer

CHAPTER 1

INTRODUCTION

Chapter 1 is the engine that drives the entire of research documentation. Hence, this section has covered and explained about research background, problem statement, research objectives, scopes and limitation for the project.

1.1 Research Background

Today the worldwide supplies of energies are mainly based on fossil fuels like coal, oil and natural gas, but their overall amounts are limited. People have already realized this energy shortage from the daily rising auto-gas price. There is no doubt that alternative sources of energy are needed in the next a few decades. Solar energy, wind energy, geo-thermal energy, biomass and hydro energies are not only renewable, they are also environmentally friendly. Among these, however, only solar energy has a large enough potential to meet the major fraction of the world's energy needs [1].

Solar cell is a device that converts light into electricity using the photovoltaic effect. Solar cell is made up of electrodes, anti-reflective coating, light absorbing materials, depletion zone and an external circuit. A nanostructured titanium dioxide (TiO_2) thin film gives high transmittance and good refractive index in the visible region with chemical stability and good durability in environments. Due to its promising features in optical, electrical, chemical and structural properties TiO_2 thin films have been widely used for many applications such as photocatalyst [2] [3], multilayer optical coating, thin film devices for solar cell and also in sensor applications [2]. Many approaches to improve the photocatalytic activity of TiO_2 have been tested, and many researchers have pointed out that the photocatalytic activity of TiO_2 generally depends on its morphology, crystal composition, crystallinity, and surface area [4]. Nanorod TiO_2 is better than planar TiO_2 as they have lower combination rate of excited electrons and they could offer direct electrical pathways for photogenerated electrons [5]. It is also reported that CuO and TiO_2 can form p-n heterojunctions, which not only greatly enhance the visible-light absorption but also improve the interfacial charge transfer and provide massive amounts of active reaction sites on the surfaces of photocatalysts [6]. Copper oxide thin films are being considered in thin film solar cells for its unique photovoltaic properties [7]. In order to fabricate highly efficient solar cells, the heterojunction process is introduced and this is proven by researches, that solar cells can be fabricated using the heterojunction process [8].

1.2 Problem Statement

Heterojunction is chosen over of homojunction because it can improve the performance of the photovoltaic devices. The best efficiency achieved in the homojunction was only around of 1% regardless of the metal deposited [9]. In order to improve the conversion efficiency, the planar TiO_2 is changed to nanorod TiO_2 as nanorod TiO_2 has lower recombination rate for excited electron–hole pair, unique optical and electric properties [5]. The nanostructures of TiO_2, such as nanorods, have attracted enormous attention because they offer direct electrical pathways for photogenerated electrons [10]. The large band gap window material with a small band gap absorber material in the heterojunction would, minimize surface recombination losses that might otherwise dominate in direct band gap materials [11]. Since rutile TiO_2 have bandgap of 3.0 eV, therefore it is suitable used in the heterojunction formation. In heterojunction phototransistors the window effect should also be effective in increasing the efficiency [12]. Previous study demonstrated the electrical power conversion efficiencies of TiO_2/Cu_2O heterojunction are still below than 2 % [13] [14] [15]. The improper electron mobility between the n and p layer is believed to be one of the reason. High mobility thin-film is reported that exploits the enhanced electron transport properties of low-dimensional polycrystalline heterojunctions [16]. The improved efficiency making thin films solar modules even more attractive as a form of power supply. It was reported that, a heterojunction should improve the performance of Cu_2O photovoltaic devices [9]. Yanping Li *et al.* had concluded that the photocatalytic activity of n-TiO_2 was significantly enhanced by combination with p-Cu_2O. This is due to the efficient p-n heterojunction as it can enhance visible-light adsorption, efficiently suppress charge recombination, improve interfacial charge transfer and especially provide plentiful active reaction sites on the surface of photocatalyst [17]. The performance of TiO_2/ Cu_2O improved as heterojunction was implemented in this research. The conversion of efficiency of the sample believed to improve as TiO_2 have nanorod structures.

1.3 Research Objectives

The objectives of this project are:

i. To fabricate nanorod TiO_2 thin film.
ii. To develop deposition method of p-Cu_2O on TiO_2 layer for heterojunction thin film development.
iii. To investigate and analyse the morphological, structural, topological and electrical properties of TiO_2/Cu_2O heterojunction thin film solar cell.

1.4 Scopes of project

In order to achieve all the objectives, the scope of this project are:

i. The nanorod TiO_2 and p-Cu_2O will be fabricated via hydrothermal and electrodeposition technique, respectively.

ii. The deposition will be carried out using nanorod TiO_2 /FTO glass substrate as a working element, platinum (Pt) as a counter element and Ag/AgCl as a reference element.

iii. The substrate is Fluorine doped Thin Oxide (FTO), a glass substrate

iv. The parameters of various duration time from 14 to 18 hours and TBOT concentration from 0.04 to 0.07 mol were conducted to optimize the performance of n-TiO_2 thin film.

v. Several parameters including deposition temperature at 40 to 60 ºC and deposition time for 30 + 30, 30 + 60, 60 + 30 and 60 + 60 minutes were used to obtain the optimized p-Cu_2O based heterostructure thin film.

vi. The structural, morphological, optical and electrical properties of TiO_2/Cu_2O heterojunction thin film solar cell will be characterized using X-ray Diffraction (XRD), Field Emission-Scanning Electron Microscope (FE-SEM), Ultraviolet-visible Spectroscopy (UV-Vis) and Four Point Probes, respectively.

1.5 Thesis layout

This thesis was discussed on fabrication of nanorod TiO_2/Cu_2O based heterostructure thin films using hydrothermal and electrodeposition method, respectively. The heterostructure was constituted by two deposition layers which n-TiO_2 and p-Cu_2O thin films. Based on the objectives and scopes of project, there were five main chapters which explaining whole fabrication process.

In Chapter 1, some introduction was briefing about research background, problem statement, research objectives and scope. Next, Chapter 2 provided essential knowledge in the area under investigation. Several literature reviews were devoted in related subtopic such as p-n heterojunction, TiO_2/Cu_2O heterostructure, hydrothermal process, electrodeposition technique, cyclic voltammetry (CV) measurement and photovoltaic concept. In addition, Chapter 3 presented fabrication of TiO_2/Cu_2O thin films flowchart which including solution and substrate preparation, hydrothermal process, electrodeposition process and characterization properties. After that, Chapter 4 showed the final results and discussion on structural, morphological, topological properties for performance both n-TiO_2 and p-Cu_2O based heterostructure thin film. Finally, conclusion was made up and recommendations for future works in this research was provided in Chapter 5.

CHAPTER 2

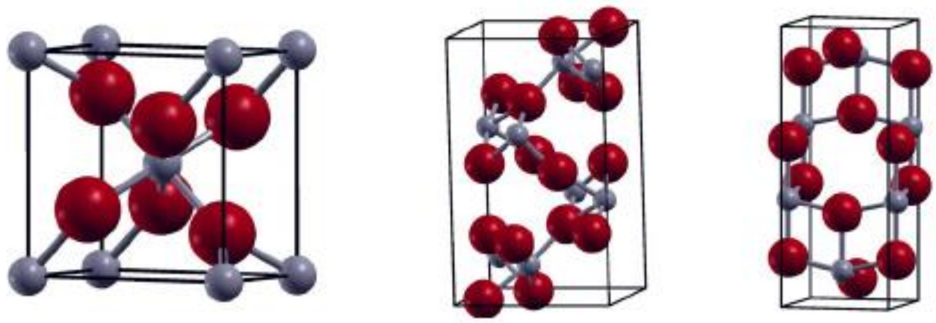
LITERATURE REVIEW

This chapter is a summary of reviews on previous studies related to this project, including fabrication process and characterization of the samples. It consists of information about the concept of photovoltaic technology, solar cell, titanium dioxide (TiO_2), copper oxide (Cu_2O), p-n heterojunction, hydrothermal process, electrodeposition technique and cyclic voltammetry (CV) measurement. The purpose of this chapter is to provide knowledge in the area under investigation and to boost ideas for further consideration.

2.1 Titanium Dioxide

It is known that TiO_2 has three crystalline phases; rutile phase (tetragonal), anatase phase (tetragonal) and brookite phase (orthorhombic) [2] [18] [19] [20]. Anatase type TiO_2 has a crystalline structure that corresponds to the tetragonal system (with dipyramidal habit) and mainly used as a photocatalyst under Ultra Violet (UV) irradiation. Rutile type TiO_2 also has a tetragonal crystal structure (with prismatic habit). Brookite type TiO_2 has an orthorhombic crystalline structure [20]. The active crystallite phases of TiO_2 are anatase and rutile although brookite is occasionally reported [19]. In nature, rutile is the most common crystal phase while brookite is scarce. Rutile phase is stable in high temperature, ranged generally from 600°C to – 1855°C, whereas anatase and brookite phases are metastable which transformed to rutile phase when annealed at high temperature. With high surface area and good electron mobility in anatase and rutile phases, respectively, it is a good idea to combine these two phases in many electronics devices such as solar cells and sensor [2]. This is also because of the crystalline structure, morphology, and crystallite size [19].

TiO_2 consists of nanostructures such as nanorods [21], nanotubes [22], nanowires [23], and mesoporous structures [24]. The photocatalytic activity of TiO2 nanoparticles is mainly determined by its crystalline phase (anatase and ructile), crystallite size, specific surface area, pore structure and crystallinity [19]. TiO_2 materials are also non-toxic [25] [8], low-cost, biocompatible [18],chemically inert and it shows the maximum light scattering with virtuality no absorption [25]. The variety of crystalline TiO_2 would produce different band gap for rutile TiO_2 of 3.0 eV and anatase TiO_2 of 3.2 eV, which will eventually determine the photocatalytic performance [26]. TiO_2 is mainly applied as pigments, adsorbents, catalyst supports, filters, coatings, photoconductors, and dielectric materials [27]. TiO_2 has been reported to be an intrinsically n-type semiconductor due to its oxygen deficiency [28] [29]. Figure 2.1 shows the primitive cell unit for rutile, brookite and anatase. Table 2.1 shows summarization synthesis of nano-TiO_2 via different methods.



(a) (b) (c)

Figure 2.1 : Primitive cell for (a) rutile, (b) brookite and (c) anatase [30]

Table 2.1: Synthesis of Nano-TiO_2 via different methods

Method	Description	Advantages/Disadvantages of Process	References
1. Chemical precipitation	• Use an environmentally friendly reaction medium • Particle size, structural phase, and morphology nanocrystallites could be easily controlled	• Produce nanoparticles with high specific surface area • Improve crystallinity • Simple process	[19]
2. CVD	• Involves the use of metal catalyst • High temperature and vacuum technique	• Process of preparation is complicated.	[5]
3. Sol-gel technique	• A wet chemical route for the synthesis and processing of inorganic and organic-inorganic hybrid materials	• Widely used • Formation of compounds that have compositional homogeneity at a molecular level, which is very important for the formation of complex oxides • When the AAO template is removed, the nanorod arrays tend to collapse due to the huge surface tension between each nanorod	[5] [31] [32]
4. Solvothermal method	• Almost identical to the hydrothermal method except that the solvent used is nonaqueous • The temperature can be elevated much higher than that in hydrothermal method.	• Normally has better control than hydrothermal methods in term of size, shape distributions and the crystallinity of the TiO2 nanoparticles • Versatile method for the synthesis of a variety of nanoparticles with narrow size distribution and dispersity	[20]
5. Hydrolysis	• Using the required precursor	• difficult to control synthesis	[19]
6. Hydrothermal	• Method of synthesis of single crystal that depends on the solubility of minerals in hot water under high pressure • Normally conducted in steel pressure vessels called autoclaves with or without Teflon liners	• Simple • Inexpensive • Highly homogenous crystalline product can be obtained directly at relatively lower reaction temperature (<150) • Fast reaction velocity	[20] [33] [25] [10] [5]

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